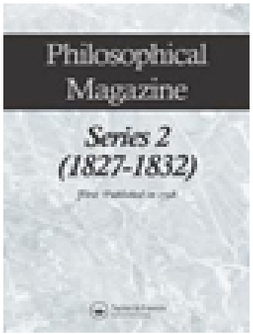

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XXXII. On a new compound of oxygen and manganese; with remarks on Dr. Turner's memoir on the oxides of that metal

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mental results, it seems to be the justest and most natural inference that can be drawn from those results.

The matter has, however, been viewed differently. The length of a degree of the parallel computed on the given spheroid is 77835 metres: but if we substitute the astronomical in place of the geodetical amplitudes, we shall have $\frac{1742''{\cdot}22}{1741{\cdot}078} \times 77835 = 77886$* metres for the mean length of a degree between Marennes and Geneva; and $\frac{3117''{\cdot}34}{3116{\cdot}121} \times 77835 = 77866$ metres† for the mean degree between Marennes and Padua. Now the differences between the mean degrees and the degree on the assumed spheroid, which are considerable, arise solely from the small differences between the geodetical and the astronomical amplitudes, or rather, as we are warranted in saying, from the errors of the astronomical amplitudes. If the small intervals of time, namely $1''{\cdot}142$ and $1''{\cdot}219$, by which the geodetical exceed the astronomical amplitudes, may be ascribed either wholly or in part to errors of observation, it will be allowed that the lengths, 51 metres and 31 metres, by which the degree on the assumed spheroid exceeds the mean degrees answering to the astronomical amplitudes, rest either on no authority, or on doubtful authority. Very little stress can therefore be laid on the new compression of the earth deduced from the combination of the mean degrees, viz. 77886 and 77866 metres, with degrees of the meridian already known. It may very well happen that this method of proceeding, instead of bringing us nearer the truth, may lead us away from it. The conclusion that follows directly and naturally from the measurement of the parallel, is in favour of the supposition that the earth is a spheroid of revolution having the compression indicated by the lengths of the meridional arcs.

Feb. 13, 1828. J. Ivory.

XXXII. *On a new Compound of Oxygen and Manganese; with Remarks on Dr. Turner's Memoir on the Oxides of that Metal.* By R. Phillips, *F.R.S. L. & E. &c.*

IN noticing Dr. Turner's "Elements of Chemistry" (Phil. Mag. and Annals, vol. i. p. 379), I have stated it as my opinion in opposition to his, that when peroxide of manganese is heated in sulphuric acid, it is converted merely into deutoxide. In a paper on the oxides of manganese, which Dr. Turner was so good as to send to me, and which has been

* *Conn. des Tems*, p. 293. † *Ibid.* p. 291.

printed in the Phil. Mag. for July and August last, he has again mentioned, that during solution in sulphuric acid the peroxide becomes protoxide; and as the result of further examination, I readily admit the accuracy of his assertion.

I employed in my first experiments, to the best of my recollection, the native oxide of manganese, which occurs, and frequently in masses of great purity, in Warwickshire; this has I believe been regarded as the peroxide of the metal. On repeating my experiments, I soon found, however, that it is not constituted as the peroxide is usually admitted to be; and in prosecuting my inquiries, I discovered that it is a compound of the metal and oxygen, which has not, as far as my researches have extended, been hitherto noticed. This mineral is of a gray colour, the tint of which is not remarkably different from that of the well-known crystallized peroxide; it is, however, less brilliant. It is much harder than the peroxide, does not soil the fingers so much, and is lighter in the proportion of 4·283 to 4·819: when reduced to powder and boiled in water, a trace of muriate of lime is discoverable.

In order to determine the state of purity of the ore, 200 grs. were treated with excess of muriatic acid, 0·64 of a grain, evidently silica, remained undissolved; sulphuretted hydrogen gas passed into the solution of muriate of manganese, threw down a dark-coloured precipitate, which, when washed and dried, weighed 1·03 grain; this yielded a deep blue solution by treatment with nitric acid and ammonia: it was therefore sulphuret of copper, and may be considered either to exist as such in the ore, or as indicating an equal weight of the peroxide. The excess of sulphuretted hydrogen being expelled by heat, the solution was colourless, and gave a perfectly white precipitate with ferrocyanate of potash.

I exposed 200 grains of the powdered ore to a strong red heat in a covered platina crucible for an hour; the loss of weight was 26·55 grains, and the mean of three experiments gave 26·52, or 13·26 per cent. As it is stated by Dr. Turner and other authorities, that peroxide of manganese, similarly treated, loses 12·122 per cent, I entertained no doubt that the ore under examination was peroxide; for the difference of 1·14 might readily be attributed to error of operation and a little accidental moisture. I next determined the quantity of oxygen separable from the ore by solution in sulphuric acid; for this purpose, I put into a glass retort 2000 grains of sulphuric acid and 200 grains of the powdered ore; the flame of a strong spirit-lamp was applied until gas ceased to be evolved; the retort was then corked, and its mouth kept under water until the sulphate of manganese was cold; the water being

being then suffered to enter, the space unoccupied by it indicated the quantity of oxygen gas remaining in the retort. There were left undissolved 7·8 grains of peroxide of manganese and silica; consequently, allowing one grain for the sulphuret of copper, 191·2 of the oxide were decomposed by the acid.

The capacity of the retort was 18 cubic inches, of which the acid and oxide occupied 5; by deducting 13 from the contents of the air-jar, amounting to 83·5 cubic inches at 60°, we have 70·5 of oxygen gas, to which are to be added 5·5 inches left in the retort, giving 76 cubic inches as the whole of the oxygen gas, yielded by 191·2 of the oxide of manganese. On repeating this experiment, I procured 76·7 inches of oxygen from 192·5 of the oxide; the mean is therefore 39·8 inches = 13·48 grains of oxygen from 100 of the ore. The peroxide of manganese being composed of 44 metal and 16 oxygen, half of which it loses in becoming protoxide, it is evident that the Warwickshire ore is very differently constituted; for as 100 : 13·48 :: 44 : 5·93, which is less than three-fourths of the oxygenth at should have been obtained from peroxide.

In Dr. Turner's paper on the oxides of manganese, already alluded to, a peculiar oxide of manganese is described under the name of Manganite; the principal facts relating to it are stated as follows: "When manganite is heated to redness it gives out 10·10 per cent of water; and the total loss from exposure to a white heat is 13·15 per cent. Deducting from the last number the amount of water, 3·05 remain as the loss in oxygen. The result of this analysis is therefore

Red oxide	86·85
Oxygen	3·05
Water	10·10
	100·00

According to this analysis, manganite contains an oxide of manganese, 89·9 parts of which yield 3·05 of oxygen, on being converted into the red oxide. An equal quantity of pure deutoxide, in undergoing a similar change, should lose 2·997 of oxygen.

"Exposed to a strong red heat and a current of hydrogen gas, 100 parts of manganite lost 19·09 parts in one experiment, and 19·07 in another. The mean is 19·08, and subtracting 10·10 as water, 8·98 remain as oxygen. According to this analysis manganite is composed of

Protoxide	80·92
Oxygen	8·98
Water	10·10
	100·00

"Now as 80·92 : 8·98 : : 36 : 3·995.

"From

"From the result of both analyses, it is apparent that manganite, in relation to manganese and oxygen, is a deutoxide.

"Also as 89·90 : 10·10 : : 4·494.

"The fourth number is so near 4·5, half an equivalent of water, that we may safely regard manganite as a compound of 80 parts, or two equivalents of the deutoxide of manganese, and 9 parts or one equivalent of water."

There are two circumstances in which the Warwickshire ore agrees very nearly with manganite, viz. in the weight which it loses by exposure to a strong, and a low red heat. I have already observed that the first-mentioned oxide loses 13·26 per cent by a strong heat, which differs only 0·11 from that lost by manganite according to Dr. Turner: by a low red heat, the ore now under consideration loses 10·2 per cent; while manganite loses 10·1. There is, however, one fact which proves that the Warwickshire oxide is not deutoxide, as manganite appears to be by Dr. Turner's analysis: it has been already shown that 44 grains of the ore now under examination, lose 5·95 of oxygen by conversion into protoxide; but an equal quantity of a compound of two atoms deutoxide =80+1 water=9 would give scarcely 4 by the same operation, for as 89 : 8 : : 44 : 4 very nearly.

More particularly to examine the source of the loss of 10·2 per cent at a low red heat, I put 200 grains of the powdered Warwickshire ore, which had been previously dried by steam, into a small coated glass retort, and heated it to redness in an open charcoal fire; an accurately weighed receiver was adapted to the retort; water came over very readily, and a little which remained near the mouth of the retort was expelled by a spirit-lamp, and condensed in the receiver.

The oxide, weighed when cold, had lost 22·4 grains; but the weight of the water was only 10·8 grains: it then occurred to me that part of the loss was owing to the extrication of oxygen, and this I found to be the case; for an ignited piece of wood immediately burnt with a vivid flame on being introduced into the receiver, although no precautions had been taken to receive any gas. I repeated this experiment with the addition of the pneumatic apparatus; the capacity of the retort was 14 cubic inches, and there was obtained a mixture of the atmospheric air of the retort and oxygen gas, amounting to 20 inches. I do not give the results of this experiment with any claim for their accuracy; but if we deduct from the gas even the whole of the atmospheric air of the retort, a considerable portion of oxygen remains; the oxide lost 20·4 grains.

It has been already mentioned that the ore loses 13·48 per cent

cent of oxygen by solution in sulphuric acid; and the water amounting to 5·4 per cent, the mineral consists of

Protoxide of Manganese	81·12
Oxygen	13·48
Water	5·40
	100·00

which are equivalent to

Manganese	63·0
Oxygen	31·6
Water	5·4
	100·0

Its atomic constitution appears to be

Two atoms Deutoxide . .	80	or Manganese . .	63·275
Two atoms Peroxide . . .	88	Oxygen	31·637
One atom Water	9	Water	5·088
	177		100·000

The agreement between the experimental results and the calculated composition seems to me sufficiently near to determine the nature of the Warwickshire ore; and it may be observed, that the atom of oxygen which the water contains would convert the two atoms of deutoxide into two of peroxide.

As Dr. Turner, in his analysis of manganite, does not appear to have suspected that it loses oxygen at a red heat, it seems to me extremely probable that the composition of manganite is similar to that of the Warwickshire oxide; and consequently, about one half of the loss, which is attributed by Dr. Turner wholly to the expulsion of water, is in fact derived from the extrication of oxygen. I am confirmed in the probability of this view of the subject, by the analyses which Dr. Turner has given of psilomelane and the *manganèse oxidé noir barytifere:* if we suppose the former to consist of 69·795 red oxide and 6·018 oxygen, instead of 7·364; and the latter to be composed of 70·967 red oxide and 6·119 oxygen, instead of 7·260 as stated,—the difficulty which Dr. Turner has observed exists in reconciling these oxides with an atomic constitution will vanish; and from the near approach to equality of the atomic weights of oxygen and water, such an error as I have proposed to correct might very readily occur. One circumstance may be observed with respect to the peculiar oxide which I have now described, viz. that it is the only one of five oxides of manganese which has not been formed artificially.

There

There are some other statements in Dr. Turner's memoir, on which I shall offer a few observations. He appears to doubt the existence of a permanent red sulphate of manganese, and to suppose, when it is obtained, that it soon becomes colourless, a precipitate being deposited in it which is the red oxide. "If the (sulphuric) acid," he observes, "which retains an amethyst tint even when cold, be again heated, the red colour speedily disappears; because the red oxide, which is dissolved in small quantity by the sulphuric acid, is then also converted into the protoxide with the evolution of oxygen gas. The red colour disappears gradually even without the aid of heat; for the solution will be found after a few days to be almost and sometimes quite colourless, when a minute quantity of red oxide has subsided to the bottom. On applying a very gentle heat the red oxide is redissolved, and the acid acquires a lively amethyst red colour. It is easy by operating in this way, to obtain satisfactory proof, that a minute portion of red oxide suffices to communicate a rich colour to a considerable quantity of sulphuric acid. The acid may be made to retain the red colour, either by diluting it with water, or by keeping it in contact with undissolved oxide."

I have frequently obtained the red sulphate of manganese, possessing, not merely an amethyst tint, but a most intense and beautiful red; and I have kept such a solution for several months without its depositing any oxide, and without keeping it in contact with undissolved oxide; and dilution with water is so far from preserving the colour of the solution, that it is instantly decomposed by it, and oxide of manganese deposited.

I have examined the circumstances under which this red sulphate is produced; and I shall take this opportunity of stating the method by which it may be formed with certainty and very readily.

Before, however, I proceed to this part of the subject, I will state the experiment upon which I have admitted that when peroxide of manganese is dissolved by sulphuric acid, it is converted into protoxide. For this purpose I used crystallized native peroxide, which contained 1·2 per cent of silica, and 0·6 of sulphuret of copper; of this 150 grains reduced to powder were heated in 2000 grains of sulphuric acid, in the mode already described when treating of the Warwickshire oxide. Without entering into minutiæ, I shall merely state, that the 147·3 grains of pure peroxide which the ore contains yielded 80 cubic inches of oxygen gas, consequently 44 would have given 8·09 grains nearly; a quantity

so

so little exceeding the weight of one atom of oxygen, that upon the result of this and a similar experiment, I have founded the admission which I have made.

I now heated similar quantities of acid and peroxide; but I stopped the operation when about 40 inches, or half the quantity obtained in the last experiment, had come over.

When water was added to the sulphate of manganese, I found that a large quantity of brown oxide of manganese, specifically very light, was diffused through it; it was evidently oxide which had in this respect at least suffered considerable change; it was separated by elutriation from 9 grains of the peroxide employed, and which remained unaltered in its properties; this altered oxide when washed and dried on a sand-heat weighed 58·8 grains.

To determine the nature of this altered oxide, 57 grains were by a strong heat converted into red oxide, by which they lost 6·8 grains, therefore 58·8 the whole quantity would have given 7·01 grains: now as 132 of peroxide lose by this treatment 16 of oxygen, 58·8 would be diminished 7·12; so that the altered oxide is evidently peroxide.

Knowing from previous experiment that red sulphate of manganese is decomposed by a large quantity of water, I repeated the last detailed experiment, but with this variation: I added to the sulphate of manganese only so much water as was sufficient to dilute it enough to allow of its being filtered through paper; by this I obtained, without regarding either the altered oxide, or that which remained unacted upon, five fluid ounces of solution of sulphate of manganese. The colour of this was so intense a red, that when diluted with twice its bulk of water, the mixture was as deep-coloured as port wine, and in tint very closely resembled it. To half the solution I added a wine pint of distilled water, precipitation immediately took place, and when slightly heated, the solution became perfectly colourless, and 3 grains of peroxide were precipitated; after the action of water potash threw down 27 grains of oxide. It has been already mentioned, that the oxide precipitated by water is peroxide; and I have found by repeated experiments, that the protoxide precipitated by potash becomes deutoxide by drying.

Assuming then, as in the former experiment, that 9 grains peroxide and silica remained unacted upon, and that about one grain of the 150 was soluble impurity, we may conclude that 140 of peroxide of manganese by losing 12·7 oxygen, were converted into deutoxide, which formed deuto-sulphate with the acid; so easily, however, is this salt decomposed by water into protoxide and peroxide, that even when employing the small

small quantity mentioned above, the proportion of deutoxide held in solution was to that decomposed, only about as 1 to 10. It is very remarkable, as Dr. Turner has observed, how small a quantity of oxide gives colour to a large quantity of solution; thus from what I have stated, it is evident that about 6 grains of deutoxide impart a colour equal in intensity to that of port wine, to a pint of solution of sulphate of manganese. The red sulphate is also very easily procured by moderately heating the artificial deutoxide in sulphuric acid. It has been already noticed that the deutoxide of manganese is obtained by merely drying the protoxide precipitated by potash; the peroxide is also easily procured by decomposing the muriate of manganese with chloride of lime; the precipitate is so extremely bulky, that a vial holding 1000 grains of water, contained, even when well shaken down, only 60 grains of it. In employing chloride of lime, the solution of muriate of manganese should be as nearly saturated as possible; for the chlorine evolved by excess of muriatic acid, occasions the acidification of a portion of the manganese. I have some reason to suppose that the peroxide thus obtained is a hydrate, containing a very small atomic quantity of water.

With respect to the red oxide of manganese, I would observe that, of all the oxides, it is the only one which suffers no change by the action of heat; the protoxide by absorbing oxygen being converted into it, while all other oxides, by evolving the same element, undergo a similar change: on this account it forms a very convenient standard in analysis; it is obtained of the reddest tint, and with least admixture of purple, by using an artificial peroxide.

In concluding, I will state what appears to be the composition of the oxides and acids of manganese at present known; premising, however, that I have made no experiments upon the two acids.

	Atoms. M. O.	M. O.
Protoxide	1+1	28+ 8
Deutoxide	2+3	28+12
Peroxide	1+2	28+16
Red oxide	3+4	28+10·66
Warwick oxide . . .	4+7	28+14
Manganous acid . .	1+3	28+24
Manganesic acid . .	1+4	28+32

XXXIII. *Reply*